The Deuterium Isotope Effect for Iminium Ion C–H Bond Insertion

By PETER T. LANSBURY* and PAUL C. BRIGGS

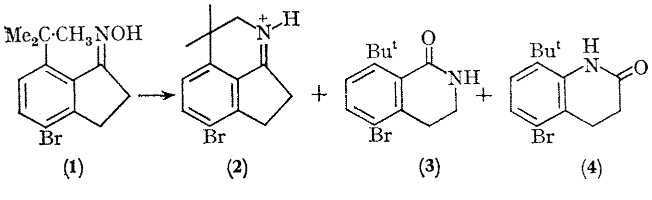
(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

Summary The univalent, electrophilic nitrogen ion generated from oxime (**1**) inserts into C–H bonds *via* the singlet state.

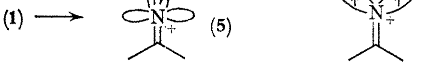
WE have previously observed that 4-bromo-7-t-butylindan-1-one oxime (**1**) reacts in polyphosphoric acid at 125—130° to produce mainly the insertion product (**2**) and lactams (**3**) and (**4**), the major isomer (**3**) resulting from net *cis* migration.[1]

Other similarly constrained 7-alkyl-indan-1-one oximes underwent analogous bond insertion and non-stereospecific Beckmann rearrangement,[2] whilst the homologous 8-alkyl-1-tetralone oximes rearranged normally without accompanying insertion.[2] Deuterium labeling studies with (**1**) ruled out a vinyl nitrene as the species responsible for (**2**)—(**4**), leaving the iminium ion as a likely intermediate.[1] The latter should be capable of existing in singlet (**5**) and triplet (**6**) states, as has been demonstrated for various nitrenes.[3]

We report the intramolecular deuterium isotope effect observed when (^{2}H$_6$-**1**) (containing two CD_3 and one CH_3 groups in the 7-t-butyl substituent) is converted to (**2**).[4] As is clear from the scheme, the ratio of C–H to C–D



(1) (2) (3) (4)

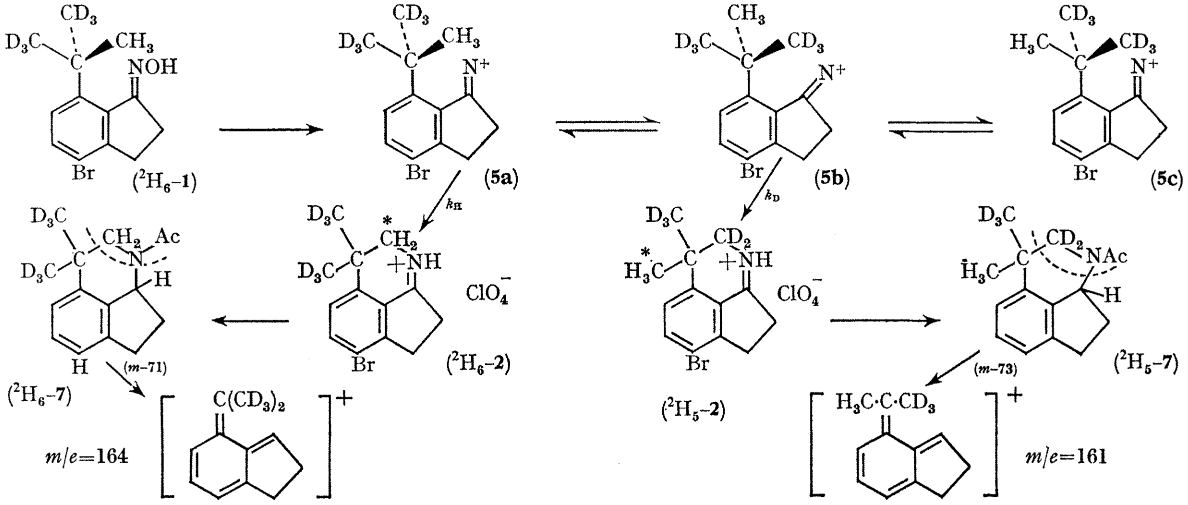


(5) (6)

insertion is available from n.m.r. spectral integration of the mixture of ($^2H_6$-**2**) (for $\diagup\overset{*}{CH_2}\diagdown N$) and ($^2H_5$-**2**) (for $C\overset{*}{H_3}$). Also, borohydride reduction of (**2**), followed by hydrogenolysis of Br and acetylation afforded labelled ($^2H_6$-**7**) and ($^2H_5$-**7**), whose ratios were assayed by mass spectral determination of $M - 71$ and $M-73$ peaks (*ca.* 0·75).‡ From six n.m.r. runs, %C–H : %C–D varied only between 0·68 to 0·72 (average 0·70). The actual isotope effect depends upon which of two as yet undistinguished situations prevails regarding the rates of conformer interconversion [assuming equal populations of (**5a**) (**5b**) and (**5c**)] *vs.* bond insertion. If conformer interconversion is faster than insertion,§ k_H/k_D is simply twice the observed ratio (there being two CD_3's), *i.e.*

$$k_H/k_D = \frac{2[(^2H_6\text{-}\mathbf{2})]}{[(^2H_5\text{-}\mathbf{2})]} = 2(0{\cdot}70) = 1{\cdot}4$$

At the other extreme, if insertion occurs faster than t-butyl group rotation, one can show that if k_H/k_D for conformer (**5a**) or (**5b**) is $\alpha/1\text{-}\alpha$, then for all conformers $2\alpha/(3-2\alpha) = 0{\cdot}70$, the observed ratio, and hence $k_H/k_D = 1{\cdot}6$.



Regardless of which isotope effect is "correct", we consider the data (as well as the chemistry) to support insertion by singlet ion (**5**) via a triangular transition state[1] (*cf.* $k_H/k_D = 1{\cdot}5$ for *singlet* $:\ddot{N}\text{-}CO_2C_2H_5$ inserting into cyclohexane[3b] versus $k_H/k_D = 4{\cdot}1$ at 160° for triplet $Ph\text{–}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}\cdot$ abstracting the tertiary hydrogen atom in isobutane).[4] This is as expected, since singlet → triplet crossing is quite slow in nitrenes,[3b] as judged from the requirement for extensive dilution to get triplet additions of $:NCO_2Et$ to olefins, and our reaction is intramolecular. Nevertheless, the presence of bromine in (**1**) could have provided for an intramolecular "heavy atom" effect[5] to make intersystem crossing quite rapid.¶ We are, attempting to generate ion (**6**) by optimizing the latter effect, in order to compare the fate of the triplet state with that of (**5**).

We thank the U.S. Army Research Office (Durham) for generous financial support.

(*Received, July* 21*st*, 1969; *Com.* 1082.)

---

† This compound, prepared as before (ref. 1), using [$^2H_6$]t-butylbenzene, from $(CD_3)_2CO$, had ⩽10% [$^2H_5$] impurity.

‡ We thank Professor D. B. MacLean of McMaster University for assistance with this determination.

§ 7-t-Butyl-indan-1-one showed no restricted rotation of the t-butyl group, on the n.m.r. time scale, down to −60°. At 120—130°, rotation is clearly rapid but whether faster than the insertion rate is difficult to ascertain.

¶ That the 4-Br substituent in (1) was unable to produce a "heavy atom" effect was indicated by finding that 7-[$^2H_6$]-butylindanone oxime gave the same C–H : C–D insertion ratio as ($^2H_6$-1) (%C–H : %C–D = 0·73 ± 0·05 for 3 runs).

[1] P. T. Lansbury, J. G. Colson, and N. R. Mancuso, *J. Amer. Chem. Soc.*, 1964, **86**, 5225.

[2] P. T. Lansbury and N. R. Mancuso, *J. Amer. Chem. Soc.*, 1966, **88**, 1205.

[3] (a) A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1967, **89**, 3184; (b) W. Lwowski and T. J. Maricich, *ibid.*, 1965, **87**, 3630; (c) W. Lwowski, "Nitrenes", Interscience, New York, 1969, ch. 7.

[4] J. H. Hall, J. W. Hill and J. M. Forgher, *J. Amer. Chem. Soc.*, 1968, **90**, 5313. Another high isotope effect for nitrogen abstraction of H atoms was observed in the Loeffler-Freytag reaction, where k_H k_D = 3·54 (E. J. Corey and W. R. Hertler, *ibid.*, 1960, **82**, 1657.

[5] J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules", Methuen, London 1963, pp. 294—300.